

MOFzyme: Enzyme Mimics of Fe/Fe-MIL-101

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Abstract

In this work, metal-organic frameworks (MOFs) Fe-MIL-101 was synthesized by hydrothermal method, and Fe/Fe-MIL-101 with different loadings was prepared. The crystal structure of the Fe/Fe-MIL-101 sample was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and specific surface area measurement (BET). Fe/Fe-MIL-101 was found to possess an intrinsic enzyme mimicking activity similar to that found in natural horseradish peroxidase (HRP). The Michaelis constant (K_m) of 5% Fe/Fe-MIL-101 with ABTS as the substrate is about 10-fold smaller than Fe-MIL-101 and about 3-fold smaller than HRP, and about 108 times less than that of CuO NPs ($K_m = 10.28$ mM), indicating a much higher affinity for ABTS than HRP and most of the peroxidase mimetics.

Keywords

Metal-Organic Frameworks (MOFs), Fe-MIL-101, 5% Fe/Fe-MIL-101, Peroxidase Mimetics

1. Introduction

Natural enzymes have attracted much attention because of their high catalytic efficiency and strong response characteristics. However, natural enzymes have many problems such as inactivation and denaturation, difficulty in purification, high cost and difficulty in storage and easily affected by environmental conditions including pH, temperature and inhibitors [1] [2]. These defects largely limit the application of enzyme. Therefore, the preparation and application of artificial mimic enzymes is a current research topic in recent years. In the past few decades, many mimic enzymes have been discovered [3] [4], for example,

cytochrome P450 mimetics [5], serine proteases mimetics [6], dioxygenase mimetics [7], phosphodiesterase mimetics [8] and so on. Among these, a large number of peroxidase mimics, such as hemin [9] [10], hemeatin [11], hemoglobin [12], cyclodextrin [13], and porphyrin [14] [15], etc, have been used for H₂O₂ and ascorbic acid detection [13] [14]. However, these peroxide mimicking enzymes have lower catalytic activity and poorer selectivity than natural enzymes. Therefore, it is necessary to work harder to design a mimetic enzyme with high catalytic activity.

Metal-organic frameworks (MOFs) are topologically formed by organic ligands and inorganic metal clusters, a type of zeolite-like crystalline porous materials, have been recently researched as new functional materials. Compared with traditional zeolite, activated carbon and other materials, it has the advantages of high specific surface area, adjustable pore structure and easy modification. It has extensively application prospects in the fields of gas storage [16], separation [17] and catalysis [18], and has attracted much attention in science and biological systems. In view of the above advantages of MOFs, we consider it to be a material suitable for simulating enzymes. Indeed, Fe-MIL-101 [19], Fe-MIL-88NH₂ [20], MIL-53(Fe) [21], MIL-100(Fe) and MIL-68(Fe) [22] were found to have the activity of peroxide mimicking enzyme. Cu-MOF [23] was synthesized for catalyzing hydrolysis of bovine serum albumin and casein by solvothermal method. Despite the many exciting and convincing developments recently, we believe that the MOF-based catalytic field is still in the development and immature stage. In this work, we make use of the novel properties of 5% Fe/Fe-MIL-101 as peroxidase mimetics to catalyze oxidation of the ABTS by H₂O₂.

2. Methods

2.1. Chemicals and Instrumentation

All commercial chemicals were used without further purification. Terephthalic acid (H₂BDC, 99%), Ferric chloride hexahydrate (FeCl₃·6H₂O, 99%), ethanol (99.5%), sodium borohydride (NaBH₄), NaOH, hydrogen peroxide (H₂O₂) were purchased from Sigma-Aldrich.

2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) were obtained from BBI (Ontario, Canada). X-ray powder diffraction (XRD) experiments were conducted on a D/max-3B spectrometer with Cu K α radiation. Scans were made in the 2 θ range 3° - 40° with a scan rate of 10° min⁻¹ (wide angle diffraction). Scanning electron microscopy (SEM) images of samples were obtained with a FEI Quanta 200FEG microscope. BET surface areas and pore volumes were measured through nitrogen adsorption/desorption measurements using a Micromeritics Tristar II surface area and porosity analyzer.

2.2. Synthesis of Fe/Fe-MIL-101

The Fe-MIL-101 is synthesized by hydrothermal method using p-dibenzoic acid

as ligand iron as metal active center [24]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.675 g) was added slowly into DMF (15 mL) solution, followed by adding H_2BDC (0.206 g). The mixture was under continuous mechanical stirring for 10 min at room temperature, and then transferred into a Teon-lined stainless steel autoclave and heated at 110°C for 20 h. The resulting brown solid was separated from the reaction medium, and purified by using the hot ethanol (70°C), the purification process was carried out several times, followed by drying in an oven (70°C , 30 min). The particles were separated by centrifuging and washed with DMF and ethanol to remove any unreacted raw materials.

2.3. Preparation of 1% Fe/Fe-MIL-101

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.0195 g) and Fe-MIL-101 (0.4 g) were dissolved in ethanol, stirred at room temperature for 1 h, centrifuged and washed 3 times in ethanol and dried under vacuum at 80°C to obtain the product 1. NaBH_4 (2 mL, 1.875 mg/mL) solution was added dropwise to the solution of product 1 (product 1:150 mg, ethanol: 10 mL, dichloromethane: 50 mL), stirred at 0°C under nitrogen for 30 min and then stirred at room temperature for 30 min. The precipitate was collected by centrifuging to obtain the product 1% Fe/Fe-MIL-101.

3% Fe/Fe-MIL-101, 5% Fe/Fe-MIL-101, and 8% Fe/Fe-MIL-101 were prepared by changing the amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ added.

2.4. Peroxidase-Like Activity of 5% Fe/Fe-MIL-101

The effect of pH, temperature, H_2O_2 concentration and ABTS concentration on the peroxidase-like activity of 5% Fe/Fe-MIL-101 was performed in a reaction volume of 3 mL of buffer solution. Buffers used in this experiment were acetate buffer (pH 4.0-6.0) and borate buffer (pH 8.0-10.0). The steady state kinetic assays of 5% Fe/Fe-MIL-101 were carried out by changing the concentration of ABTS at a fixed concentration of H_2O_2 or vice versa at 50°C . After 5 minutes of reaction, the absorbance of the reaction solution was measured at a wavelength of 420 nm using a Shi-madzu UV-2450 spectrophotometer. The kinetic parameters were calculated based on the equation:

$$v = V_{\max}([S] / (K_m + [S])) \quad (1)$$

where v is the initial velocity, V_{\max} is the maximal velocity, $[S]$ is the concentration of the substrate, and K_m is the Michaelis constant.

3. Results and Discussion

3.1. The Characterization of Fe/Fe-MIL-101

The X-ray diffraction (XRD) pattern of the as-synthesized Fe-MIL-101 is shown in **Figure 1(a)**. The diffraction peaks all corresponded to the products synthesized in the literature [24] and generally consistent with the pattern calculated from the crystallographic data in this reference. Moreover the diffraction peaks position of obtained Fe/Fe-MIL-101 by different iron loadings are the same as Fe-MIL-101, but the intensity of the diffraction peaks are weaker than

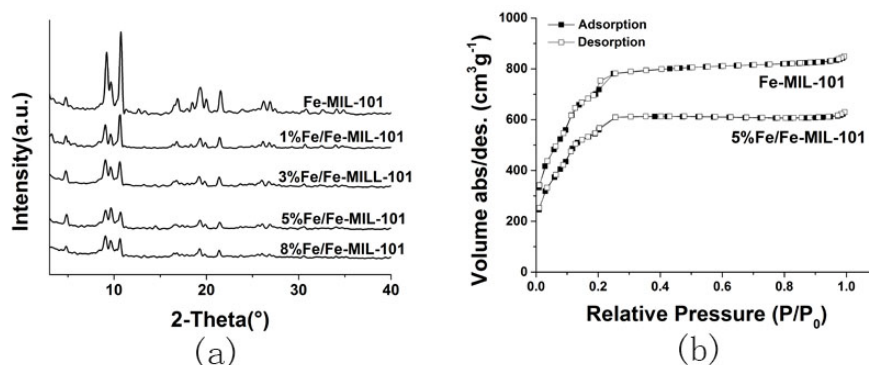


Figure 1. (a) XRD patterns of the Fe-MIL-101 and Fe/Fe-MIL-101. (b) N₂ adsorption/desorption isotherm pore distribution of 5% Fe/Fe-MIL-101 and Fe-MIL-101.

Fe-MIL-101. The adsorption – desorption isotherms of 5% Fe/Fe-MIL-101 are of type I (**Figure 1(b)**), indicating the presence of a microporous network. Compared with Fe-MIL-101, the BET specific surface area of the experimentally synthesized 5% Fe/Fe-MIL-101 material decreased from 2737 m²/g to 2148 m²/g, and the pore volume decreased from 0.75 cm³·g⁻¹ to 0.51 cm³·g⁻¹, the average pore size decreased from 2.51 nm to 2.35 nm, the reduction of specific surface area, pore size and pore volume probably due to the blockage of material pores by the loaded iron. SEM images show that 5% Fe/Fe-MIL-101 has a typical octahedron morphology like Fe-MIL-101 (**Figure 2(a)** and **Figure 2(b)**), but the surface is rough, and it is obvious that there are small solid iron particles on the surface. All of the results mentioned above confirmed that 5% Fe/Fe-MIL-101 was successfully synthesized.

3.2. Peroxidase-Like Activity of 1% Fe/Fe-MIL-101

In order to study the peroxidase-like activity of 1% Fe/Fe-MIL-101, the conventional catalytic oxidation of the peroxidase substrate ABTS in the presence of H₂O₂ was tested. As shown in **Figure 3**, in the absence and presence of H₂O₂, which displayed a negligible absorption at the maximum absorbance of 420 nm, indicating that ABTS could not be oxidized by H₂O₂ without any catalysts. In contrast, 1%Fe/Fe-MIL-101 could catalyze the oxidation of ABTS by H₂O₂ (**Figure 3**), with a maximum absorbance at 420 nm, indicating that 1% Fe/Fe-MIL-10 gave higher response and showed catalytic activity toward ABTS oxidation in the presence of H₂O₂.

Table 1 mainly compares the absorbance values of Fe/Fe-MIL-101 with iron loadings at load ratios R = 0.01, R = 0.03 and R = 0.05, R = 0.08, respectively. A significant effect of the load ratio on the absorbance values is visible, the absorbance value are growing with increasing load ratio (R = 0.01 - 0.05), however, the absorbance value is decreasing when the load ratio is increased to 0.08. Since the absorbance value of 5% Fe/Fe-MIL-101 was the largest, 5% Fe/Fe-MIL-101 was selected as the experimental object in the next experiment.

The peroxidase-like catalytic activity of 5% Fe/Fe-MIL-101 was studied by

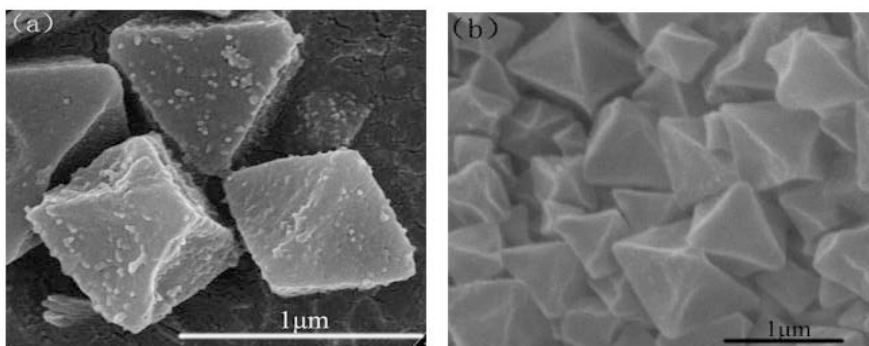


Figure 2. (a) SEM images of the 5% Fe/Fe-MIL-101 and (b) Fe-MIL-101.

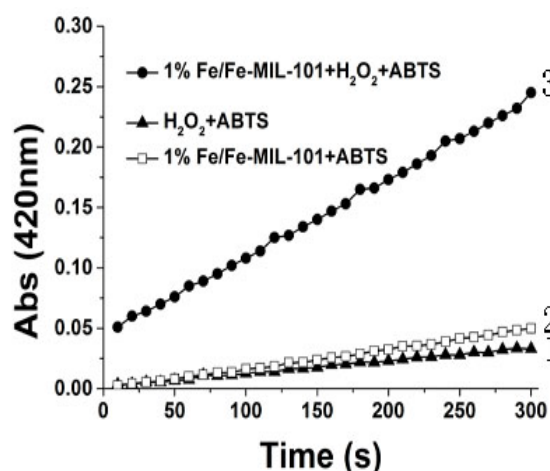


Figure 3. Time-dependent absorbance changes at 420 nm in the presence of (1) H₂O₂ and ABTS, (2) ABTS and 1% Fe/Fe-MIL-101, (3) H₂O₂ and ABTS and 1% Fe/Fe-MIL-101.

Table 1. Comparison of absorbance values of different catalyst.

Catalysts	1% Fe/Fe-MIL-101	3% Fe/Fe-MIL-101	5% Fe/Fe-MIL-101	8% Fe/Fe-MIL-101
Absorbance Values	0.245	0.311	0.404	0.331

selecting the substrates ABTS and H₂O₂ as a model reaction system. The peroxidase-like activity of 5% Fe/Fe-MIL-101 was measured at different pH (3.0-9.0) and various temperature (30 °C - 50 °C) (**Figure 4(a)** and **Figure 4(b)**). As can be seen from **Figure 5**, the pH 4.0 and 45 °C were the optimal reaction condition, which are very similar to the values for HRP [25].

3.3. Kinetic Analysis

We used steady-state kinetics to further study the peroxidase-like catalytic mechanism and kinetic parameters of 5% Fe/Fe-MIL-101. The kinetic data was collected by changing the concentration of one substrate at a fixed concentration of the other substrate. Within the concentration range of TMB and H₂O₂ used,

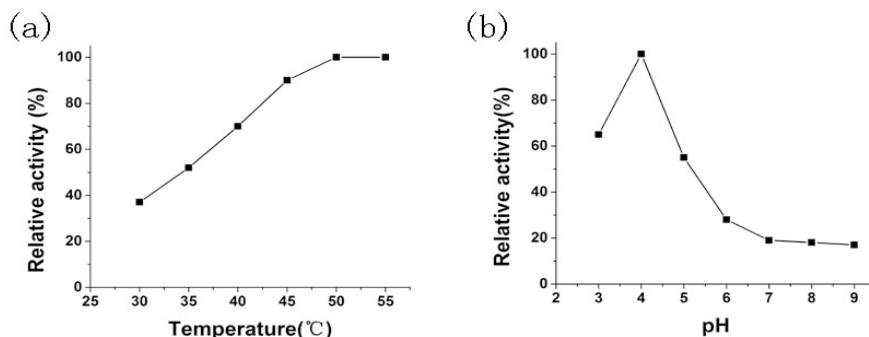


Figure 4. The peroxidase-like activity of the 5% Fe/Fe-MIL-101 hybrid is dependent on the temperature (a) and pH (b).

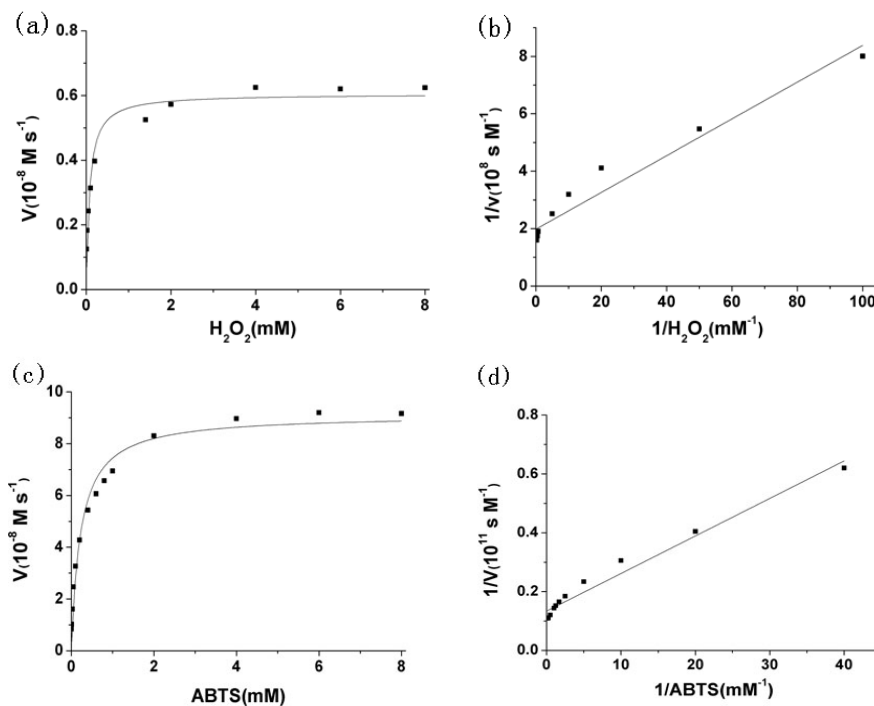


Figure 5. ((a) and (c)) Steady-state kinetic assays of 5% Fe/Fe-MIL-101. (a) The concentration of TMB was fixed and the H_2O_2 concentration was varied in acetate buffer at pH 4.0 (b) double-reciprocal plots of the activity of 5% Fe/Fe-MIL-101. (c) The concentration of H_2O_2 was fixed and the ABTS concentration was varied in acetate buffer at pH 4.0. (d) double-reciprocal plots of the activity of 5% Fe/Fe-MIL-101.

typical Michaelis-Menten curves were observed (**Figure 5**). A Lineweaver-Burk plot can be obtained with a nearly linear relationship (**Figure 5(b)** and **Figure 5(d)**), from which important kinetic parameters can be derived (**Table 2**). The kinetic parameters, such as the Michaelis-Menten constant (K_m) and maximum initial velocity (V_{\max}) were from a Lineweaver-Burk plot. The Michaelis constant, K_m , the smaller the K_m value, the stronger the affinity of the enzyme to the substrate, and the higher the catalytic activity of the enzyme. As shown in **Table 2**, the K_m value of 5% Fe/Fe-MIL-101 (0.095 mM) with ABTS as the substrate under the optimum conditions (20 mM acetate buffer, pH 4.0) was about 3-fold

Table 2. Comparison of the Michaelis constant (K_m) of 5% Fe/Fe-MIL-101 and other enzyme mimics at pH 4.0.

Catalysts	Substrates	K_m (mM)	V_{max} ($M \cdot s^{-1}$)	Reference
5% Fe/Fe-MIL-101	ABTS	0.095	5.376×10^{-11}	This work
5% Fe/Fe-MIL-101	H ₂ O ₂	2.7	5.051×10^{-11}	This work
Fe-MIL-101	ABTS	0.916	1.603×10^{-11}	[26]
Fe-MIL-101	H ₂ O ₂	3.7	2.498×10^{-11}	[26]
CuO NPs	ABTS	10.28		[27]
CuO NPs	H ₂ O ₂	120.3		[27]
HRP	ABTS	0.319		[25]
HRP	H ₂ O ₂	5.44		[25]

lower than HRP (0.319 mM), and this value is about 108 times less than that of CuO NPs ($K_m = 10.28$ mM) and about 10-fold lower than Fe-MIL-101 (0.916 mM), indicating a much higher affinity for H₂O₂ than HRP and most of the peroxidase mimetics at pH 4.0.

4. Conclusion

The present study demonstrates that the 5% Fe/Fe-MIL-101 exhibited excellent peroxidase-like activity, catalyzing the oxidation of ABTS in the presence of H₂O₂. The Michaelis constant (K_m) of 5% Fe/Fe-MIL-101 with ABTS as the substrate is about 10-fold smaller than Fe-MIL-101 and about 3-fold smaller than HRP, and about 108 times less than that of CuO NPs ($K_m = 10.28$ mM), indicating a much higher affinity for ABTS than HRP and most of the peroxidase mimetics. The above findings will open such catalytic systems for a variety of potential applications in biological systems in the future because of their ease of preparation, high activity and stability.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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